

AD-A190 651

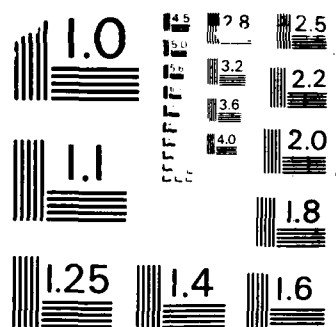
THE KINETICS OF CONTACT NOISE IN γ -ALUMINA UTAH 1/1
UNIV SALT LAKE CITY DEPT OF PHYSICS C K KUO ET AL
JAN 88 TR-15-ONR N00014-82-K-0603

UNCLASSIFIED

F/G 20/1

NL





1a REPORT SECURITY CLASSIFICATION
UNC

2a SECURITY

AD-A190 651

1b RESTRICTIVE MARKINGS

DTIC FILE COPY

2b DECLASSIFICATION/DOWNGRADING SCHEDULE

3 DISTRIBUTION AVAILABILITY OF REPORT
APPROVED FOR PUBLIC RELEASE AND SALE.
DISTRIBUTION UNLIMITED.

4 PERFORMING ORGANIZATION REPORT NUMBER(S)

ONR TECHNICAL REPORT #15

5 MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION

PHYSICS DEPARTMENT

6b OFFICE SYMBOL
(If applicable)

7a NAME OF MONITORING ORGANIZATION

OFFICE OF NAVAL RESEARCH

6c ADDRESS (City, State, and ZIP Code)

UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH 84112

7b ADDRESS (City, State, and ZIP Code) Robert J. Silverman
Adm. Contracting Officer, ONR Resident Rep.,
University of Washington, Univ. Dist. Bldg.,
Rm 315, 1107 N.E. 45th Str., Seattle WA 98105-

8a NAME OF FUNDING SPONSORING ORGANIZATION

OFFICE OF NAVAL RESEARCH

8b OFFICE SYMBOL
(If applicable)

ONR

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

4731

N00014-82-K-0603

8c ADDRESS (City, State, and ZIP Code)

Leader, Chemistry Div., Assoc. Dir. of
Mathematics & Physical Sciences,
800 N. Quincy St., Arlington VA 22217

10 SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NOPROJECT
NOTASK
NOWORK UNIT
ACCESSION NO

11 TITLE (Include Security Classification)

THE KINETICS OF CONTACT NOISE IN NaBETA"ALUMINA. (UNCLASSIFIED)

12 PERSONAL AUTHOR(S)

Chu Kun Kuo and James J. Brophy

13a TYPE OF REPORT

Technical

13b TIME COVERED

FROM 1987 TO Jan 1988

14 DATE OF REPORT (Year, Month, Day)

January 1988

15 PAGE COUNT

Twelve (12)

16 SUPPLEMENTARY NOTATION

17 COSATI CODES

FIELD

GROUP

SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Diffusion noise, conductivity fluctuations, superionic
conductors, beta alumina ceramics, and single crystals.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The kinetics of interfacial chemical reaction noise at sodium amalgam and NaI propylene carbonate contacts to NaBeta"Alumina are examined by determining the time and temperature dependence of the noise. The rate constant for the reaction noise is larger for amalgam contacts and increases with sodium concentration in both cases. The noise is thermally activated with an activation energy of 0.5eV, which is similar to that of bulk diffusion noise in NaBeta"Alumina.

DTIC
ELECTE
JAN 27 1988
S D

20 DISTRIBUTION AVAILABILITY OF ABSTRACT

☐ UNCLASSIFIED UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION

UNCLASSIFIED

22a NAME OF RESPONSIBLE INDIVIDUAL

22b TELEPHONE (Include Area Code)

22c OFFICE SYMBOL

THE KINETICS OF CONTACT NOISE IN Naβ"ALUMINA

Chu Kun Kuo and James J. Brophy

Department of Physics
University of Utah
Salt Lake City, Utah 84112

[illegible]

This document has been approved for public release
and sale; its distribution is unlimited.

THE KINETICS OF CONTACT NOISE IN Na β "ALUMINA

by

Chu Kun Kuo* and James J. Brophy
Physics Department
University of Utah
Salt Lake City, Utah 84112

Abstract

The kinetics of interfacial chemical reaction noise at sodium amalgam and NaI propylene carbonate contacts to Na β "alumina are examined by determining the time and temperature dependence of the noise. The rate constant for the reaction noise is larger for amalgam contacts and increases with sodium concentration in both cases. The noise is thermally activated with an activation energy of 0.5eV, which is similar to that of bulk diffusion noise in Na β "alumina.

INTRODUCTION

Contact noise ascribed to chemical reactions at the interface between liquid electrodes to Na β "alumina has been observed for several electrode materials, both ohmic and blocking (1,2). In general, the contact noise levels decrease with time such that Nyquist noise of the bulk solid electrolyte and diffusion noise of the mobile ions can be detected. In the case of pure mercury contacts, a chemical reaction rate constant of 4500 sec⁻¹ is observed at room temperature and the noise is associated with amalgamation reactions at the interface (3).

All electrode materials examined to date also exhibit chemical reaction noise having a much smaller rate constant (4). The kinetics of this reaction are reported here for sodium amalgam and NaI in propylene carbonate electrodes to Na β "alumina, both of which are known to produce stable, low noise contacts after ageing.

EXPERIMENTAL PROCEDURE

Commercial sodium β "alumina ceramic samples (5), $1 \times 1 \times 0.2 \text{ cm}^3$ and $1 \times 0.5 \times 0.2 \text{ cm}^3$, are carefully polished with #500 carborundum paper, baked in air and then provided with sodium amalgam or propylene carbonate solution electrodes by epoxying the ceramic into the sides of plastic tubes. Amalgams of different concentrations are prepared by electrolyzing a concentrated NaCl solution. Similarly, weighed amounts of NaI are dissolved in a known volume of propylene carbonate to achieved differing sodium concentrations in the electrode material. Voltage fluctuations of the newly prepared contacts are measured at the input of a PAR 113 preamplifier and analyzed digitally using an A/D conversion and FFT system. The time and temperature dependence of the noise is determined at several frequencies in order to evaluate the behavior of the noise decay.

RESULTS AND DISCUSSION

Typical noise spectra of sodium amalgam and NaI propylene carbonate contacts to Na β "alumina ceramics are shown in Figure 1 for different times after preparation. The slope of -2 suggests a Lorentzian noise spectrum associated with a non-equilibrium reaction having a single relaxation time

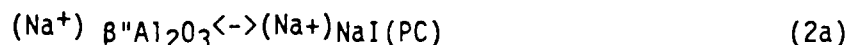
(1,2). After ageing, the noise of both contact materials decreases sufficiently for Nyquist noise of the bulk electrolyte to be observed at frequencies above about 10 Hz. Before attaining the equilibrium state, the amalgam electrode always shows much higher noise levels than the propylene carbonate. Low noise contacts of both electrode systems can be established in a few hours for all the concentrations investigated here except for most the dilute amalgam (0.19 mole% Na), for which the low frequency excess noise is still observable after ageing twenty-four hours.

The interfacial reaction noise for both electrodes decays exponentially with time, Figure 2. The voltage fluctuations at a given frequency as a function of the ageing time t after contact preparation can be written as

$$S(f,t) = A\exp(-kt) \quad (1)$$

where A and k are constants dependent upon concentration. Table 1 lists experimentally determined values for different concentrations of sodium in the liquid electrodes. Clearly, the rate constant in the case of the amalgam electrodes is much greater than that for the NaI propylene carbonate contacts, and both increase with sodium concentration. Also, the largest rate constant, $3.16 \times 10^{-3} \text{sec}^{-1}$, places the characteristic frequency of the Lorentzian spectrum at $k/2\pi = 5 \times 10^{-5} \text{ Hz}$, well below the range of the experimental measurements illustrated in Figure 1. In the concentration interval investigated here, both electrodes show a linear relationship between the rate constant and the concentration of sodium species in the liquid electrodes, Figure 3, indicating a first order reaction.

As illustrated in Figure 4, the rate constant is thermally activated. The data yield an activation energy of 0.5 eV/mole, which is close to the activation energy of bulk current noise attributed to diffusion of the mobile sodium ions (6). The similar activation energies suggest that there exists the same dominating mechanism in both processes. Since the sodium ions are the sole ionic species mobile within the Na β "alumina, they must be involved in the reaction responsible for forming equilibrium contacts. Possible reactions, then, are illustrated in Equations (2a) and (2b) in which an interaction is assumed to exist between the sodium ions in the Na β "alumina and the sodium species in the electrodes:



The first order reaction derived from the concentration dependence of noise decay rate shows that the dominating reaction is a unimolecular process. The reaction rates for the two types of contacts are different at the same sodium concentration, which is likely to result from the dissimilar chemical state of the Na species in the amalgam compared to the propylene carbonate solution.

Figure 4 also illustrates the temperature dependence of the pre-exponential factor A in Equation (1), which corresponds to the non-equilibrium reaction noise at $t=0$. The activation energy is 0.58 eV.

However, further calculation by inserting the extrapolated noise and rate constant into Equation (7) of Ref. 2,

$$S(V,f) = \frac{4Nk^3e^2Z_c^2}{k^2+\omega^2} \quad (3)$$

yields unreasonably high contact impedances. On the other hand, we can insert the temperature-dependent terms into Equation (3) to calculate the activation energy of the impedance involved in the charge transport for the non-equilibrium reaction,

$$S(V,f,T) = \frac{4N(T)k^3(T)e^2Z^2(T)}{k^2(T)+\omega^2} \quad (4)$$

At frequencies much higher than the turnover frequency,

$$\begin{aligned} S(V,f,T) &\approx \frac{4N(T)k^3(T)e^2Z^2(T)}{\omega^2} \\ &= \frac{4N_0k_0^3e^2Z_0^2(T)}{\omega^2} \exp(-E_N-3E_k+E_z) \end{aligned} \quad (5)$$

where E_N , E_k and E_z stand for the activation energy for reaction species, rate constant and impedance, respectively. N_0 , k_0 and Z_0 are the pre-exponential factors. After inserting the activation energies 0.58 eV, $E_N=0.75$ eV and $E_k=0.5$ eV into Equation (5), we obtain $E_z=0.84$ eV. This value is reasonable if both the ion transport processes in bulk solid electrolyte and at the electrolyte-electrode interface are concerned.

CONCLUSIONS

1. The chemical reaction noise generated at the interface between sodium amalgam or NaI propylene carbonate solution contacts to Na β "alumina decays exponentially with time and equilibrium low noise contacts can be attained by ageing the contacts for several hours.
2. The rate constant for the interfacial reactions increases linearly with sodium concentration in the electrodes, which indicates a first-order reaction.
3. The activation energy of the contact noise rate constant in the amalgam electrode system is 0.5 eV, which is close to that associated with bulk current noise in Na β "alumina.
4. The contact noise is attributed to the interactions between the sodium species at the electrolyte-electrode interface.

* On leave from Shanghai Institute of Ceramics, Chinese Academy of Science.

REFERENCES

1. J. J. Brophy and S. W. Smith, J. Appl. Phys. 56, 801 (1984).
2. J. J. Brophy and S. W. Smith, J. Appl. Phys. 58, 381 (1985).
3. C. K. Kuo and J. J. Brophy, Solid State Ionics, 25, 000 (1987).
4. C. K. Kuo and J. J. Brophy, Sixth International meeting on Solid State Ionics, Garmisch-Partenkirchen, Sept., 1987.
5. Obtained from Ceramatec, Inc., Salt Lake City, Utah 84119.
6. C. K. Kuo and J. J. Brophy, to be published.

Table 1. Noise decay parameters of contacts to Na β "alumina

Concentration Mole % Na	Frequency Hz	Pre-exponential Factor A (v^2/Hz)	Rate Constant, k 10^{-3} Sec^{-1}
Sodium amalgam			
0.19	10	3.52×10^{-12}	0.702
1.24	10	1.02×10^{-12}	1.38
2.34	10	6.82×10^{-13}	1.71
4.96	10	9.79×10^{-14}	3.16
NaI propylene carbonate solution			
0.4	1	2.22×10^{-14}	0.277
	0.1	3.62×10^{-12}	0.282
4.2	1	1.46×10^{-14}	0.328
	0.1	1.52×10^{-12}	0.332
8.6	1	1.70×10^{-14}	0.448
	0.1	3.35×10^{-13}	0.460

FIGURE CAPTIONS

Figure 1. Contact noise spectra for sodium amalgam and NaI propylene carbonate solution to Na β alumina ceramics. The times shown are the ageing times after contact preparation.

Figure 2. Typical noise decay data and calculated curves from Equation (1).

Figure 3. Rate constant vs sodium concentration in electrodes.

Figure 4. Temperature dependence of the reaction rate constant and prefactor A for the 1.24 mole% amalgam contact to Na β alumina.

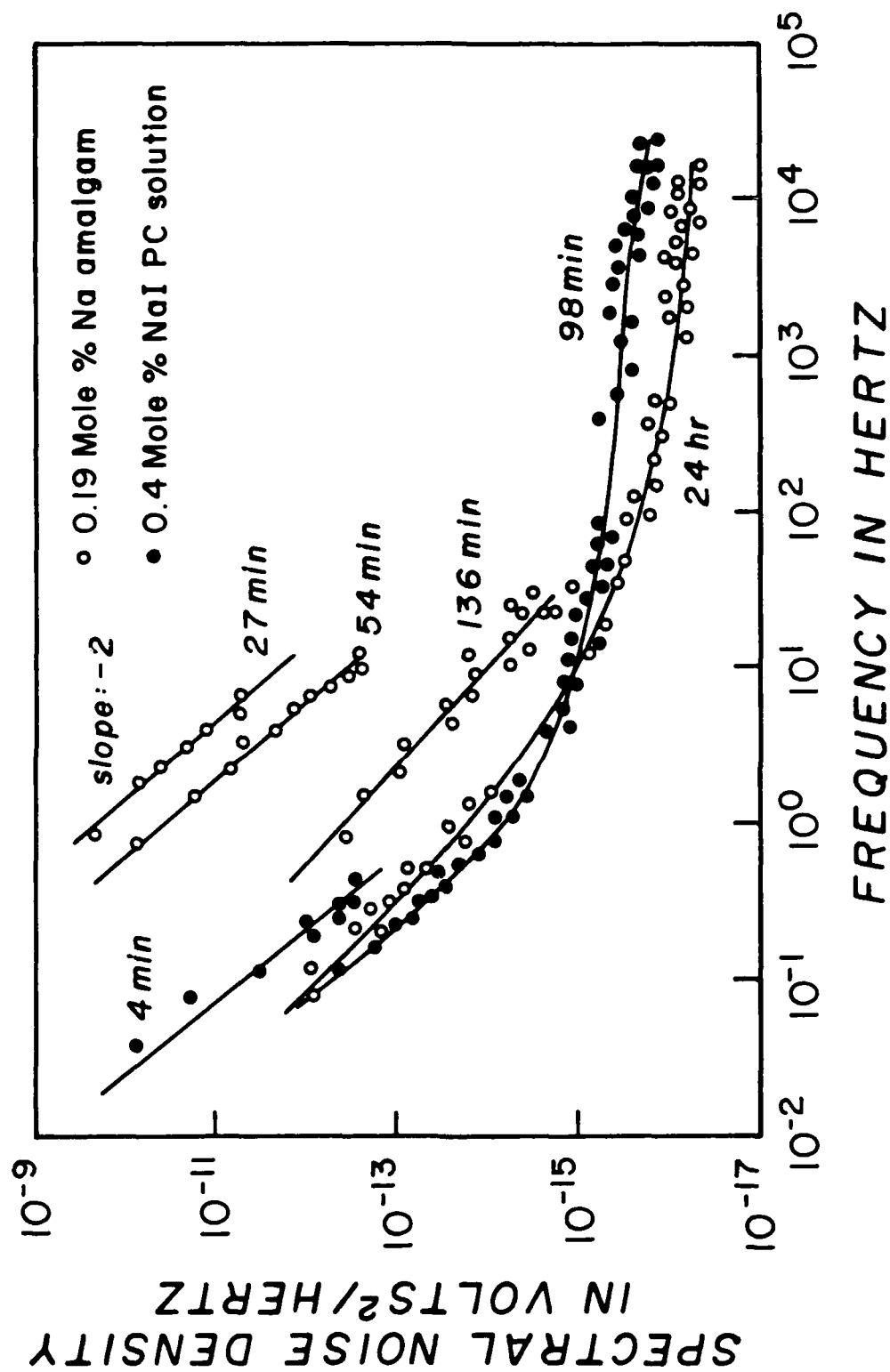


Figure 1

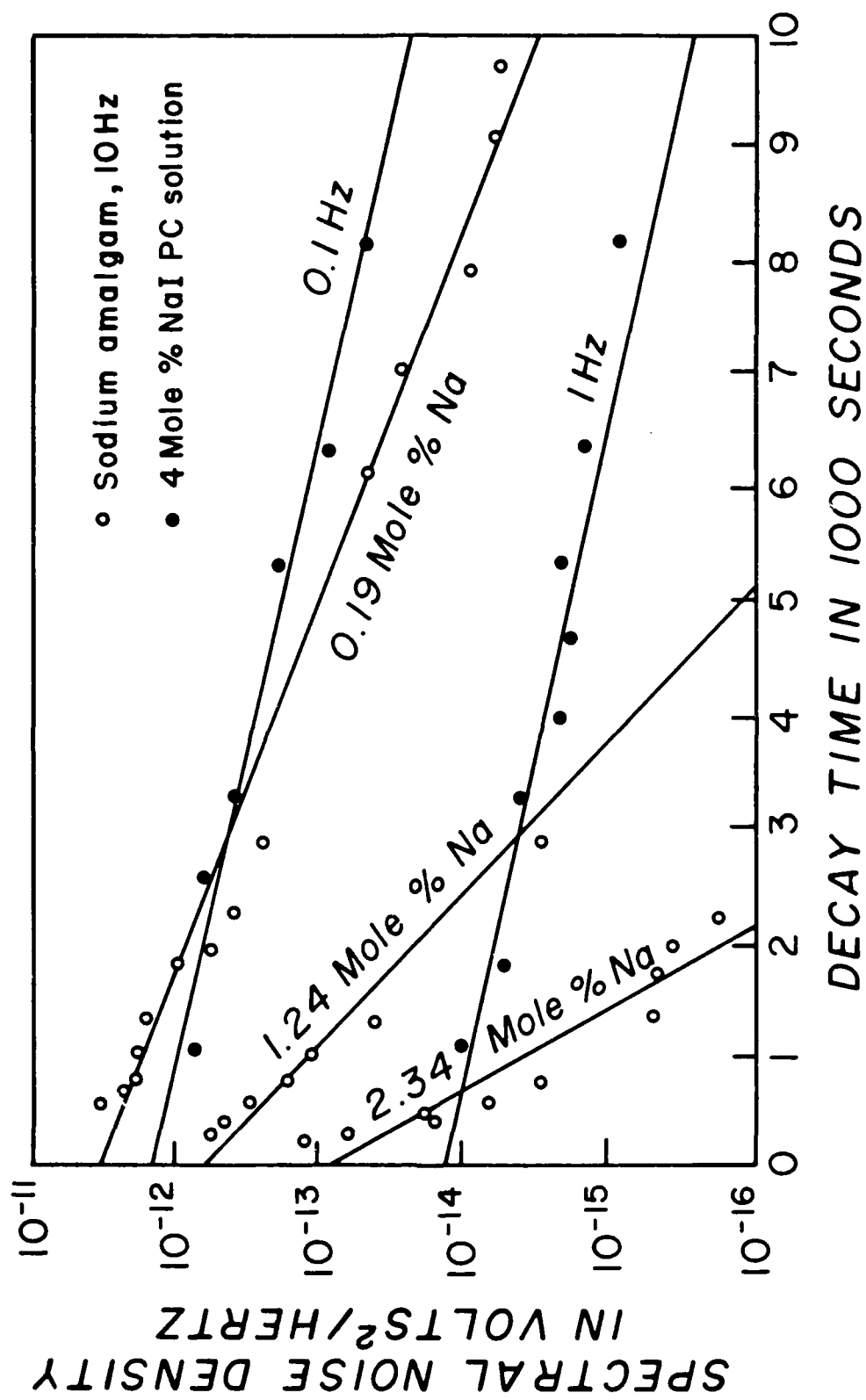
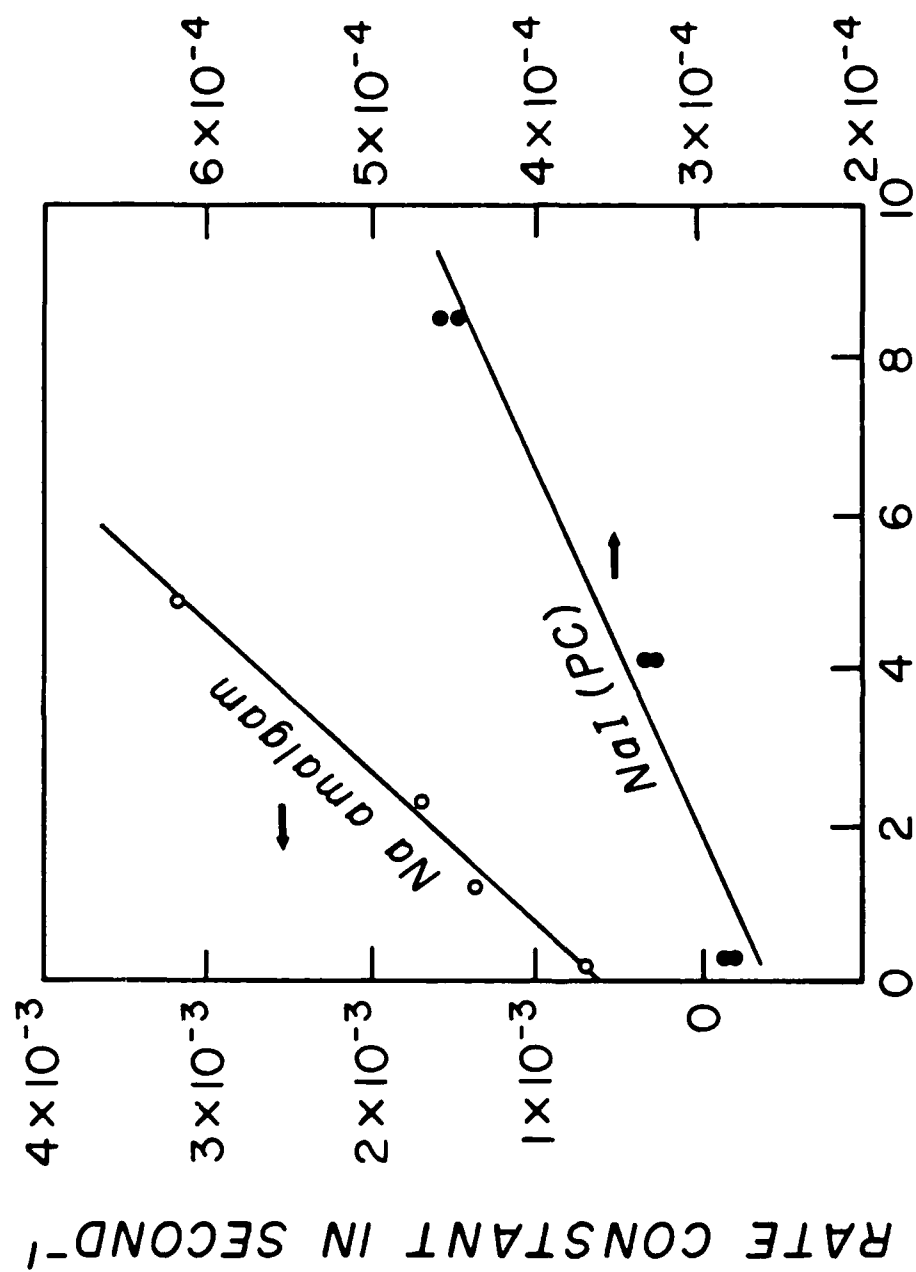


Figure 2



MOLE % Na IN AMALGAM OR NaI IN
PROPYLENE CARBONATE SOLUTION

Figure 3

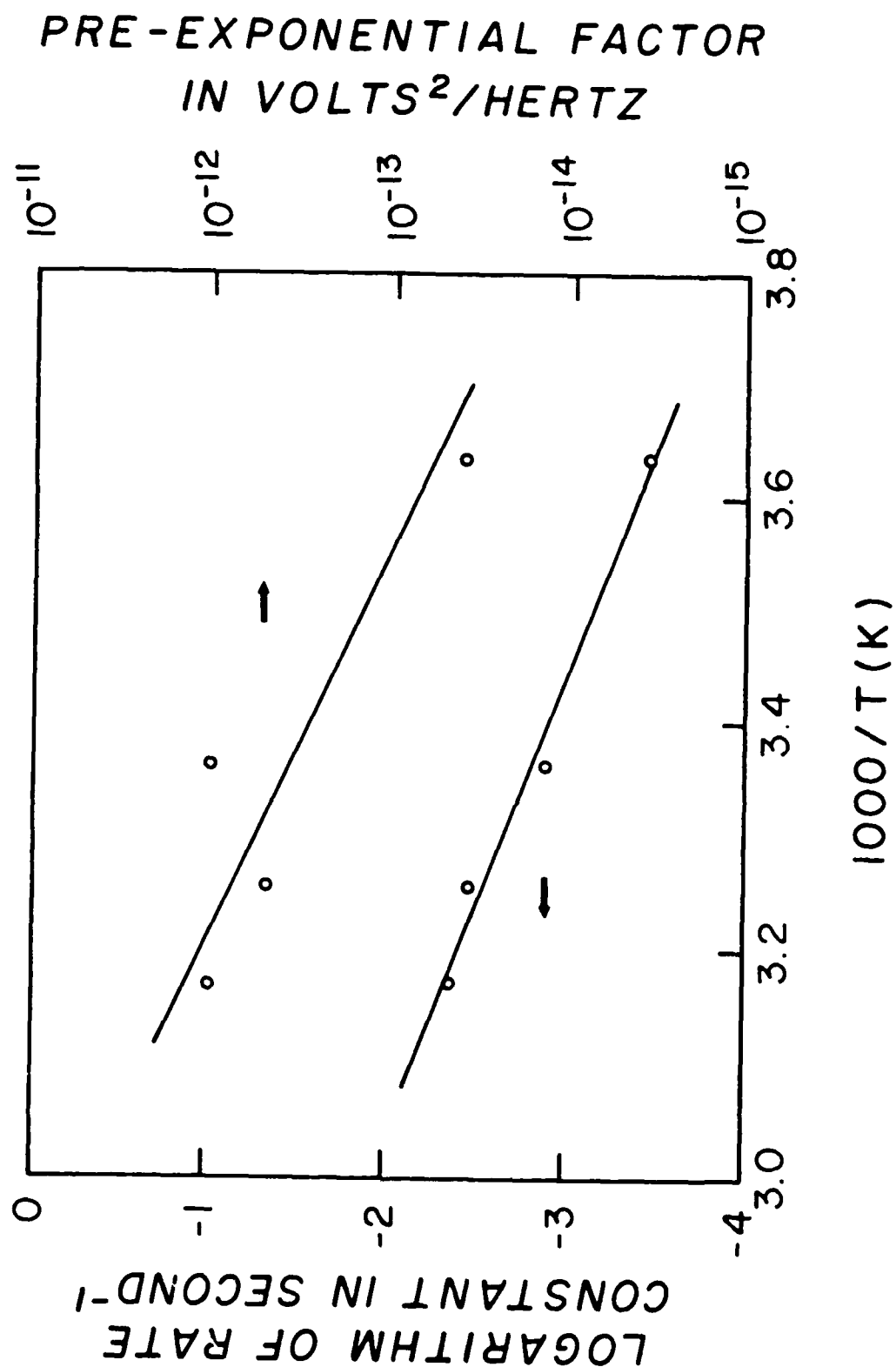


Figure 4

END
DATE
FILMED
DTIC
4/88